Crossover in the nature of the metallic phases in the perovskite-type $R\mathrm{NiO_3}$

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We have measured the photoemission spectra of $\mathrm{Nd_{1-x}Sm_xNiO_3}$, where the metal-insulator transition and the Néel ordering occur at the same temperature for $x \lesssim 0.4$ and the metal-insulator transition temperature (T_{MI}) is higher than the Néel temperature for $x \gtrsim 0.4$. For $x \leq 0.4$, the spectral intensity at the Fermi level is high in the metallic phase above T_{MI} and gradually decreases with cooling in the insulating phase below T_{MI} while for $x > 0.4$ it shows a pseudogap-like behavior above T_{MI} and further diminishes below T_{MI}. The results clearly establish that there is a sharp change in the nature of the electronic correlations in the middle ($x \sim 0.4$) of the metallic phase of the $R\mathrm{NiO_3}$ system.

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Many $3d$ transition-metal compounds undergo a metal-insulator transition as a function of temperature, carrier concentration, band width and so on.[1,2] In these systems, electron correlation plays an important role. V_2O_3, $NiS_{2-x}Se_x$, NiS and $R\mathrm{NiO_3}$ (R: rare earth) are well-known *bandwidth-controlled* metal-insulator transition systems. They undergo a transition from an antiferromagnetic insulator to a paramagnetic metal under high pressure or under "chemical pressure". To understand their phase diagrams from a microscopic point of view is one of the major goals in the studies of strongly correlated systems and much theoretical effort has been made so far along this direction.[3,4] In V_2O_3 (Ref. 5) and $NiS_{2-x}Se_x$ (Ref. 6), the metallic phase exists on the lower temperature side of the paramagnetic insulating phase as predicted theoretically[3] and as expected from the large magnetic entropy in the paramagnetic insulating phase. On the other hand, the phase diagram of $R\mathrm{NiO_3}$ has a peculiar feature that the metallic phase exists on the higher temperature side of the paramagnetic insulating phase as shown in Fig. 1.[7]

The perovskite-type oxide $R\mathrm{NiO_3}$ belongs to the charge-transfer regime of the Zaanen-Sawatzky-Allen (ZSA) diagram[8], and its ligand-to-metal charge-transfer energy Δ is smaller than the $3d$-$3d$ Coulomb repulsion energy U ($\Delta < U$). Hence its band gap is given by $\sim \Delta - W$, where W is the band width. W depends on the Ni-O-Ni bond angle or the tolerance factor [$\equiv d_{R-\mathrm{O}}/\sqrt{2}d_{\mathrm{Ni-O}}$], which depends on the rare-earth ionic radius. Hence, whether the band gap is open ($\Delta \gtrsim W$) or closed ($\Delta \lesssim W$) is determined by the deviation of the Ni-O-Ni bond angle from the ideal value 180°. As illustrated in Fig. 1, the least distorted $LaNiO_3$, which has the perovskite structure with a weak rhombohedral distortion, is a paramagnetic metal at all temperatures. The other $R\mathrm{NiO_3}$ members, which have the orthorhombic $GdFeO_3$-type structure, undergo a temperature-induced metal-insulator transition. The metal-insulator transition and the antiferromagnetic ordering occur at the same temperature for R = Pr and Nd, while the metal-insulator transition temperature (T_{MI}) is higher than the Néel temperature (T_N) for the compounds with R = Sm and other small rare earths. As a result, the metallic phase exists on the higher temperature side of the paramagnetic insulating phase. The boundary between these two types of phase transitions is located between $NdNiO_3$ and $SmNiO_3$.

Recently, Vobornik *et al.*[9] reported that the temperature dependence of photoemission spectra near E_F in the insulating phase is different between $NdNiO_3$ and $SmNiO_3$, which is probably related with the different magnetoresistance behaviors reported by Mallik *et al.*[10]

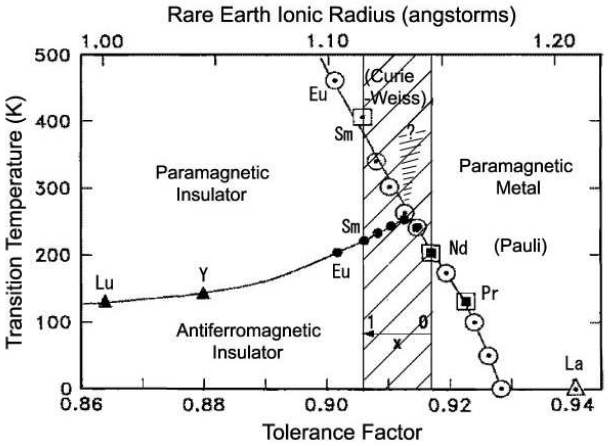

FIG. 1: Phase diagram of $R\mathrm{NiO_3}$ taken from Ref. 7. The hatched area indicates the composition range for which we have measured the photoemission spectra and the dashed lines indicates a new crossover or phase boundary line in the metallic phase proposed in this study.

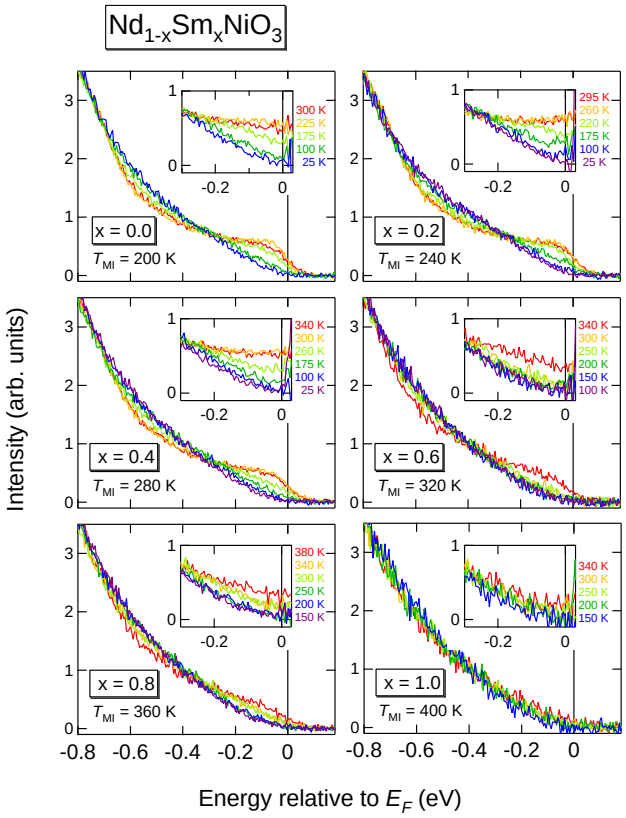

FIG. 2: Temperature dependence of photoemission spectra in $Nd_{1-x}Sm_xNiO_3$ for various x's. Inset for each panel shows spectra divided by the Fermi-Dirac function.

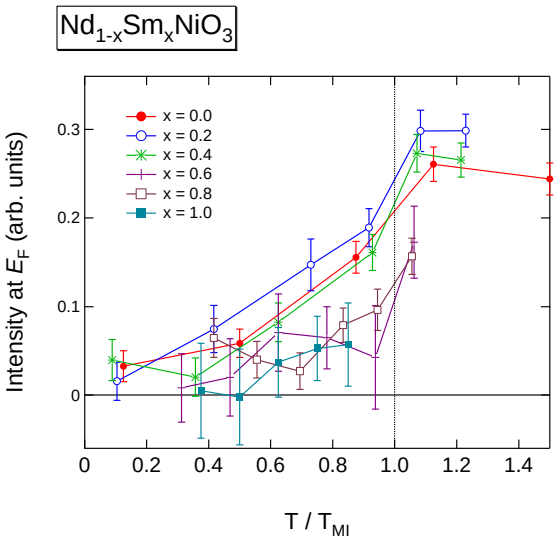

FIG. 3: Photoemission intensity at E_F as a function of normalized temperature T/T_{MI}.

In the $Nd_{1-x}Sm_xNiO_3$ system, $T_{MI} > T_N$ for $x \gtrsim 0.4$, while $T_{MI} = T_N$ for $x \lesssim 0.4$ (Fig. 1). In this Rapid Communicattion, we report on a systematic photoemission study of $Nd_{1-x}Sm_xNiO_3$ as a function of x and temperature and reveal quite different behaviors between $x \leq 0.4$ and $x > 0.4$. Based on this result, we propose that there is a phase boundary or a crossover line within the metallic phase, which separates two different kinds of metallic phases in the RNiO$_3$ system.

Preparation and characterization of polycrystalline $Nd_{1-x}Sm_xNiO_3$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) are described elsewhere.[10] The T_{MI} was measured by the differential scanning calorimetric method, and was 199.5 K for $NdNiO_3$ and 400.2 K for $SmNiO_3$. For the T_{MI} of the intermediate compounds, we have linearly interpolated between $NdNiO_3$ and $SmNiO_3$ according to Ref. 11. Photoemission measurements were carried out using a VSW hemispherical analyzer and a VG He discharge lamp. The He I (21.2 eV) resonance line was used for excitation. The total energy resolution was set to about 30 meV. Clean surfaces were obtained by repeated *in situ* scraping at each measurement temperature. The base pressure of the spectrometer was better than 1×10^{-10} Torr.

Figure 2 shows the photoemission spectra of $Nd_{1-x}Sm_xNiO_3$ at various temperatures. All the spectra have been normalized to the integrated intensity in the indicated energy range, that is, from - 0.8 eV to 0.2 eV. The results for $NdNiO_3$ and $SmNiO_3$ are consistent with Vobornik *et al.*'s results,[9] i.e., the spectra of $NdNiO_3$ show a high intensity at E_F above T_{MI} and decreasing intensity below T_{MI}. The intensity continuously decreases with decreasing temperature even well below T_{MI}. The spectra of $SmNiO_3$ show a weaker temperature dependence below T_{MI}. As for $Nd_{1-x}Sm_xNiO_3$, the spectra for $x = 0.2$ and 0.4 show a strong temperature dependence similar to $NdNiO_3$. They show clear spectral weight transfer from the region - (0-0.3) eV to - (0.3-0.6) eV in going from above T_{MI} to well below it. The spectra for $x = 0.6$ and 0.8 also show similar spectral weight transfer but the overall intensity is weak similar to $SmNiO_3$. In the $x = 0.6$, 0.8, and 1.0 compounds, the T_N is different from the T_{MI}, and no remarkable change has been observed at T_N. The temperature dependence of the intensity at E_F plotted in Fig. 3 clearly indicates the contrasting behavior between $x \leq 0.4$ and $x > 0.4$. Since the boundary between $T_{MI} = T_N$ and $T_{MI} > T_N$ is located at $x \sim 0.4$, the result implies that the electronic structure is different depending on whether $T_{MI} = T_N$ or $T_{MI} > T_N$.

In order to remove the effect of the Fermi-Dirac distribution function and to deduce the experimental "density of states" (DOS), we have divided the spectra by the Fermi-Dirac distribution function broadened with a Gaussian corresponding to the experimental resolution as shown in the inset of each panel of Fig. 2. For $x \leq 0.4$, the experimental DOS above T_{MI} is almost flat or weakly increases with energy. Just below T_{MI}, the DOS is reduced, but remains finite at E_F, indicating a pseudogap opening of 0.1 - 0.2 eV. On the other hand, the spectra for $x > 0.4$ is pseudogap-like already above T_{MI}.

Figure 4 (a) and (b) shows the Fermi-Dirac function-

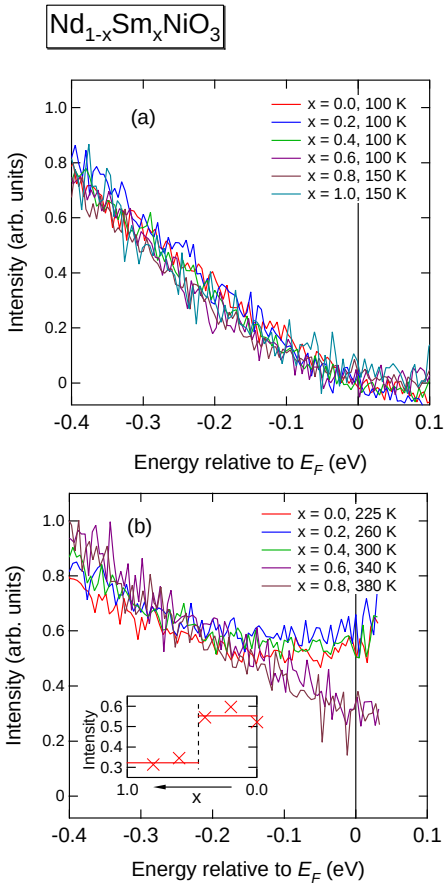

FIG. 4: Composition dependence of the photoemission spectra $Nd_{1-x}Sm_xNiO_3$ (a) Spectra taken at the lowest temperatures. (b) Spectra taken just above T_{MI}. Inset shows the intensity at E_F just above T_{MI} as a function of x.

divided spectra taken at the lowest temperatures and just above T_{MI}, respectively. The spectra taken at the lowest temperatures are identical for all x's. This suggests that the ground state is essentially the same for all x's, i.e., in the same antiferromagnetic insulating state. This is in accordance with the fact that the magnetic structure is the same between $NdNiO_3$ (Ref. 12) and $SmNiO_3$ (Ref. 13). Also, charge disproportionation was recently found in $NdNiO_3$,[14] which implied that it is present in all $RNiO_3$ ($R \neq$ La) because it had been already found in other $RNiO_3$ with small R (R = Ho, Y, Er, Tm, Yb and Lu).[15] On the other hand, the spectra above T_{MI} is quite different between $x \leq 0.4$ and $x > 0.4$. The spectra for $x \leq 0.4$ is nearly flat around E_F whereas the spectra for $x = 0.6$ and 0.8 show a weak pseudogap-like behavior. This indicates that the paramagnetic metallic phase is different between $x \leq 0.4$ and $x > 0.4$. As shown in the inset of Fig. 4 (b), the intensity at E_F just above T_{MI} sharply changes at $x \sim 0.4$. From these results, we consider that a phase boundary or a sharp crossover line exists within the high-temperature metallic phase at $x \sim 0.4$.

There have been some reports which indicate that the metallic phase may be different between $NdNiO_3$ and $SmNiO_3$. According to the magnetic susceptibility measurement of $NdNiO_3$[16] and $SmNiO_3$,[17] the metallic phase of $NdNiO_3$ is Pauli-paramagnetic after the subtraction of the rare-earth local-moment contribution, while that of $SmNiO_3$ is Curie-Weiss like. This result would indicate that the metallic phase of $NdNiO_3$ is essentially the same as that of Pauli-paramagnetic $LaNiO_3$, while conduction electrons in the metallic phase of $SmNiO_3$ show local moment behavior. Due to the existence of the local moment, the metallic phase of $SmNiO_3$ would have a large magnetic entropy. If the entropy of the local moments plus that of the conduction electrons in the metallic phase exceed the entropy of the local moments in the paramagnetic insulating phase, the metallic phase can exist on the higher temperature side of the paramagnetic insulating phase across the first-order metal-insulator phase boundary. In the $Nd_{1-x}Sm_xNiO_3$ system, the band width becomes narrower with Sm content, making Δ/W larger. We propose that with Sm content, the Ni $3d$ electrons become more strongly correlated and the local magnetic moment is induced.

Finally, we comment on the origin of the strong temperature dependence of the spectra in the insulating phase. Granados *et al.*[18,19] and Blasco and Garcia[20] have reported that hysteresis below T_{MI} extends to a wide temperature range up to 70 K from the transport and calorimetric measurement and proposed that the metallic and insulating phases coexist over this temperature range. The temperature dependence of the photoemission spectra in the insulating phase may be related to this unusually strong hysteresis. We may attribute these strong hysteretic features to disorder such as oxygen nonstoichiometry and/or rare-earth atom vacancies, which cannot be avoided in this kind of materials. In a system where both disorder and electron correlation effect are important, the spectra may show an unusual temperature dependence as reported by Sarma *et al.*[21] on disorder-induced metal-insulator transition in $LaNi_{1-x}M_xO_3$ (M = Mn, Fe, and Co). According to them, while an insulating compound has a finite gap at E_F at very low temperatures, the gap closes at elevated temperature. Competing or cooperative behaviors between electron correlation and disorder have not been investigated so far and have to be clarified in future.

In conclusion, we have studied the temperature-dependent electronic structure of $Nd_{1-x}Sm_xNiO_3$ by photoemission measurements. While the spectra at the lowest temperatures are identical for all x's, the spectra above T_{MI} show a pseudogap behavior for $x > 0.4$, different from the spectra of a typical metal for $x \leq 0.4$. It appears that the appearance of the pseudogap is related with the appearance of local magnetic moment in the metallic phase of $x > 0.4$. We propose that the nature of the metallic state is different between these two composition ranges caused by a change in the strength of electron correlation between the two regions.

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